

Plume optical transmission studies of explosive boiling and lift-off of a thin 2-propanol layer on a laser-heated Si substrate

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Using a KrF laser for explosive boiling and lift-off of a thin 2-propanol layer on a laser-heated Si substrate of interest for laser-assisted particle removal, plume velocities were measured in air by an optical transmission technique as a function of laser fluence and the alcohol layer thickness. The plume velocities were found to diminish inversely proportional to the thickness of the 2-propanol layer. This dependence was explained on the basis of the momentum conservation rule, assuming explosive expansion of the superheated alcohol layer under spinodal conditions.

Laser cleaning was recognized in the early 90s to be enhanced with the ablation of a thin transparent liquid layer deposited onto the contaminated critical surface before the pulsed laser irradiation.¹ During the last decade the basic mechanism of this steam laser cleaning (SLC) process was found to be concerned with explosive boiling and evaporation of a whole superheated liquid layer together with contaminants in the form of a vapor-droplet plume and simple estimates of cleaning force have been performed.^{2,3} Nevertheless, superheating of an \sim micron-thick liquid layer commonly used looks questionable on a nanosecond time scale and, moreover, it is to be noted that SLC thresholds have not been studied yet systematically as a function of a liquid layer thickness. Furthermore, another realistic cleaning scenario may be proposed to be concerned with a viscous drag force exerted to contaminating stationary particles by lifting-off of the whole liquid layer removed in a way similar to, e.g., the laser-induced forward transfer (LIFT)⁴, MALDI or some other phenomena⁵. Unlike the boiling threshold of the corresponding liquid, in this case the lift-off velocity and cleaning force should be sensitive to the inertia (thickness) of the liquid layer, decreasing with growth of the layer thickness.⁵ Apparently, this new SLC scenario should be examined further experimentally in details. In this paper we report using of an optical transmission technique to measure velocities for a 2-propanol plume, obtained at various laser fluences by KrF laser heating of a Si substrate with pre-deposited variable layers of the alcohol.

For example, an \sim 248-nm, \sim 20-ns KrF excimer laser beam (for example, Lambda Physik, LPX 210) was apertured in its central part by an \sim 1-cm wide vertical slit and was imaged by a cylindrical lens ($f \approx 10$ cm) at normal incidence onto an \sim 0.25-mm thick Si(100) wafer with a pre-deposited 2-propanol layer (Fig.1). The laser beam has nearly rectangular and gaussian fluence, F , distributions in the horizontal (X) and vertical (Y) directions (see insets in Fig.1), respectively,

with the characteristic dimensions of $x \approx 5$ and $\sigma_y^{1/2} \approx 1.5$ mm. Laser energy (~ 0.2 J/pulse ($\pm \sim 3\%$) after the aperture) was attenuated by color filters (for example, color filters manufactured by Corning Glass Works) and was measured by splitting off a part of the beam to a pyroelectric detector (for example, a pyroelectric detector manufactured by Gentec ED-500). A dosing system described elsewhere^{1,6} includes a source of pressurized nitrogen with a triggered valve, connected to a bubbler immersed in a glass flask filled with heated 2-propanol and directed to the Si surface through a heated output nozzle. The dosing system (gas pressure of ~ 0.7 bar, flask and nozzle temperatures of ~ 44 °C, dosing pulse of ~ 0.1 - 0.5 s) was employed to deposit a homogeneous liquid layer of a variable thickness $L \approx 0.2$ - 2.5 μm onto the Si wafer placed at a distance of ~ 5 cm from the nozzle. Deposition and a thickness of the liquid layer were controlled in a real time by observing the temporal interference fringes of optical reflectance, $R(\sim 633$ nm, $\sim 30^\circ$, s -pol), of a s -polarized HeNe laser beam focused on the center of the irradiated area at oblique incidence of $\sim 30^\circ$ [Fig.2(a)]. The heating excimer laser was fired ~ 0.05 s after the real end of each deposition step. As the plume propagated nearly along a normal to the Si wafer, another continuous HeNe laser beam was tightly focused (waist diameter of ~ 0.08 mm) with an ~ 5 -cm focal length lens in front of a center of a rectangular KrF laser spot on the wafer to probe a plume transmission, $T(\sim 633$ nm), in a transverse direction to the plume path at various distances Z from the wafer. The HeNe laser and focusing lens were mounted on a one-dimensional stage and shifted perpendicularly to the Si wafer plane with a step of ~ 0.25 mm, while a fast photodiode, detecting the transmitted HeNe radiation, was adjusted manually at each probe distance. For example, a Le-Croy 9360 storage oscilloscope triggered by an electrical pulse from a fast photodiode, detecting a scattered part of the excimer beam from the aperture slit, was used to record plume transmission transients and to measure the laser pulse energy for each pulse using the calibrated triggering

photodiode. The gas valve and excimer laser were triggered manually in a single-shot mode with the corresponding delays using a pulse generator (for example, a pulse generator manufactured by Stanford Research Systems DG 535).

For example, the transient transmission $T(\sim 633 \text{ nm})$ of 2-propanol plumes [Fig.2(b)] was probed at different distances from the Si wafer at various liquid layer thickness for laser fluences $F \approx 0.31\text{-}0.64 \text{ J/cm}^2$ above the explosive boiling threshold of the substance on a Si surface of 0.15 J/cm^2 , but well below the ablation threshold of Si, about 1.4 J/cm^2 .⁷ Comparing to the water plume studied earlier,⁶ these plumes were much shorter (less than $\sim 1 \text{ mm}$ relative to about 3 mm for the water plume) and were much more sparse, as is shown in Fig.2(b), where $T(\sim 633 \text{ nm})$ varies only $\sim 10\text{-}20\%$, depending on $Z \approx 0.25\text{-}0.5 \text{ mm}$, in comparison with $40\text{-}80\%$ drop of $T(\sim 633 \text{ nm})$ for water plumes at $Z \approx 0.5\text{-}2.5 \text{ mm}$.⁶ The $T(\sim 633 \text{ nm})$ acquisition for 2-propanol plumes was really casual at $Z > \sim 0.5 \text{ mm}$, where $T(\sim 633 \text{ nm})$ dips become weaker and broader in time because of three-dimensional rarefaction, dispersion, vaporization and other instabilities in the plume visualized elsewhere,³ and so was for 2-propanol films thinner than $\sim \mu\text{m}$.

Velocities, V_0 , of 2-propanol plumes were obtained measuring a time-of-flight, t_D , of these plumes to a HeNe probing distance [Fig.2(b)] and making a linear fit for the resulting $Z\text{-}t_D$ trajectories, presented for different experimental conditions in Fig.3(a). The resulting V_0 values of $\sim 10\text{-}40 \text{ m/s}$ for alcohol droplets [Fig.3(b)] are very low relative to supersonic velocities expected for condensation products formed during adiabatic expansion of a molecular vapor, thus confirming the assumption of lift-off of the 2-propanol liquid layer as whole, resulting from its explosive boiling. To note, a viscous drag force in air does not affect considerably these plumes until the characteristic distances of $\sim 2\text{-}3 \text{ mm}$ measured for water plumes earlier.⁶

Furthermore, the V_0 values vary inversely proportional to L [Fig.3(b)] with the slope of $\sim 1.1 \pm 0.2$, resulting in the asymptotic $V_{0\max} \sim 1.6$ km/s at L value close to the thickness of the superheated alcohol layer, $L_{\text{dep}} \sim (\chi\tau)^{1/2} \sim 0.01$ μm , where χ is the thermal diffusivity of 2-propanol and τ is the laser pulse length, but remain nearly constant at fluences of ~ 0.43 and ~ 0.64 J/cm², i.e. well above the boiling threshold, in a good agreement with previous measurements.⁶ The $V_{0\max}$ value is comparable with the longitudinal sound velocity $C_l \approx 1.2$ km/s for 2-propanol at \sim ambient conditions,⁸ according to an estimate of the thermal expansion velocity $V_{\text{exp}} \sim C_l \times (\Delta V/V_0)$ of the superheated alcohol layer near the spinodal curve. In the van der Waals approximation, the molar volume increases $(\Delta V/V_0) \approx 0.5$ -1.5 times at positive pressures along the spinodal curve till the critical point,⁹ thus resulting in the supersonic expansion velocities $V_{\text{exp}} \approx V_{0\max}$. Explosive thermal expansion and boiling of the superheated liquid layer under spinodal conditions imparts a mechanical momentum to the top cold liquid layer, acting as a vapor “piston”. The latter momentum can be found using the momentum conservation rule in the form $L_{\text{dep}} \times V_{\text{exp}} = L \times V_0$, where V_0 is the kinematical velocity of the whole cold liquid layer (or the plume), scaling as $1/L$ in agreement with the theoretical predictions⁵ and experimental measurements of water plume velocities,⁶ and of photoacoustic signals in air in the case of water-confined ablation of Si.¹⁰

In conclusion, resulting from explosive boiling of a thin 2-propanol layer on a Si substrate heated by a KrF laser, lift-off of the layer was detected in air in the form of a plume, using an optical transmission technique and plume velocities were measured as a function of the alcohol layer thickness and laser fluence. The plume velocities are decreasing inversely proportional to the total thickness of the alcohol layer, starting from the value comparable with the longitudinal sound velocity of 2-propanol fluid under ambient conditions. This dependence may be explained

on the basis of the momentum conservation rule, assuming explosive expansion of the superheated alcohol layer under spinodal conditions.

The following references are incorporated herein by reference for appropriate teachings of additional details, features, and/or technical background.

¹ K. Imen, J. Lee, and S.D. Allen, *Appl. Phys. Lett.* **58**, 203 (1991); A.C. Tam, W.P. Leung, W. Zapka, and W. Ziemlich, *J. Appl. Phys.* **71**, 3515 (1992).

² N. Do, L. Klees, A.C. Tam, P.T. Leung, and W.P. Leung, *J. Appl. Phys.* **74**, 1534 (1993); H.K. Park, D. Kim, C.P. Grigoropoulos, and A.C. Tam, *J. Appl. Phys.* **80**, 4072 (1996); O. Yavas, A. Schilling, J. Bischof, J. Boneberg, and P. Leiderer, *Appl. Phys. A* **64**, 331 (1997); Y.F. Lu, Y. Zhang, Y.H. Wan, and W.D. Song, *Appl. Surf. Sci.* **138-139**, 140 (1999); X. Wu, E. Sacher, and M. Meunier, *J. Appl. Phys.* **87**, 3618 (2000); M. Mosbacher, M. Bertsch, H.-J. Muentzer, V. Döbler, B.-U. Runge, D. Baeuerle, J. Boneberg, and P. Leiderer, *SPIE Proc.* (2nd International Symposium on Laser Precision Microfabrication, 16-18 May 2001, Singapore) (to be published).

³ M. She, D. Kim, and C.P. Grigoropoulos, *J. Appl. Phys.* **86**, 6519 (1999).

⁴ T. Sano, H. Yamada, T. Nakayama, and I. Miyamoto, *Appl. Surf. Sci.* **186**, 221 (2002).

⁵ Y. Dou, L.V. Zhigilei, N. Winograd, and B.J. Garrison, *J. Phys. Chem.* **105**, 2748 (2001); Y. Dou, L.V. Zhigilei, Z. Postawa, N. Winograd, and B.J. Garrison, *Nucl. Instrum. Meth. Phys. Res. B* **180**, 105 (2001).

⁶ S.I. Kudryashov, and S.D. Allen, *J. Appl. Phys.* (to be published).

⁷ X. Xu, C.P. Grigoropoulos, and R.E. Russo, *Appl. Phys. Lett.* **65**, 1745 (1994); S. Zhu, Y.F. Lu, and M.H. Hong, *Appl. Phys. Lett.* **79**, 1396 (2001).

⁸ I.S. Grigor'ev, and E.Z. Meilikhov, *Fizicheskie Velichini (Physical Quantities*, Energoatomizdat, Moscow, 1991), Chaps. 5-15 (in Russian).

⁹ V.P. Skripov, E.N. Sinitsyn, P.A. Pavlov, G.V. Ermakov, G.N. Muratov, N.V. Bulanov, and V.G. Baidakov, *Thermophysical Properties of Liquids in the Metastable State* (Gordon and Breach, New York, 1988).

¹⁰ S. Zhu, Y.F. Lu, and M.H. Hong, Appl. Phys. Lett. **79**, 1396 (2001).

FIG.1. Experimental setup for transient plume transmission studies: BS - beam splitter, L – focusing lenses, PD – fast photodiodes, target – Si wafer on a three-dimensional stage. Insets: (a) laser power temporal dependence of the KrF laser, (b) gaussian distribution of fluence F in the vertical (Y) direction.

FIG.2. (a) R(~ 633 nm, $\sim 30^\circ$, s-pol) transients for different dosing times of ~ 0.1 – 0.5 s exhibiting interference fringes in a homogeneous 2-propanol layer onto a Si wafer (arrows show the laser firing moment); (b) 2-propanol plume transmission transients at $Z \approx 0.25$ mm (1) and $Z \approx 2.5$ mm (2) at $F \approx 0.64$ J/cm² and $L \approx 2.5$ μ m (arrows show the arrival time of the plume at the probed distance).

FIG.3. (a) Characteristic Z - t_D trajectories at laser fluences of ~ 0.64 J/cm² (black symbols, $L \approx 0.4$ and ~ 2.4 μ m) and ~ 0.43 J/cm² (open symbols, $L \approx 1.5$ and ~ 2.4 μ m) with their linear fits; (b) dependence of plume velocity V_0 on L fitted by a linear regression: ~ 0.64 J/cm² (black symbols), ~ 0.43 J/cm² (open symbols). The slope and asymptotic value $V_{0\max}$ of the fitting curve are presented in the figure. Note that data for ~ 0.4 μ m thick films were not used in the linear fit because V_0 for only two Z - t_D points could be measured.

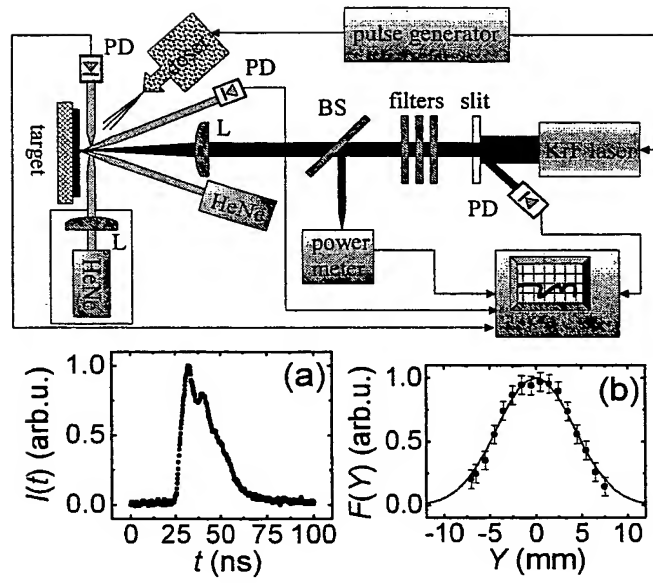


Fig.1, S.I. Kudryashov, Appl. Phys. Lett.

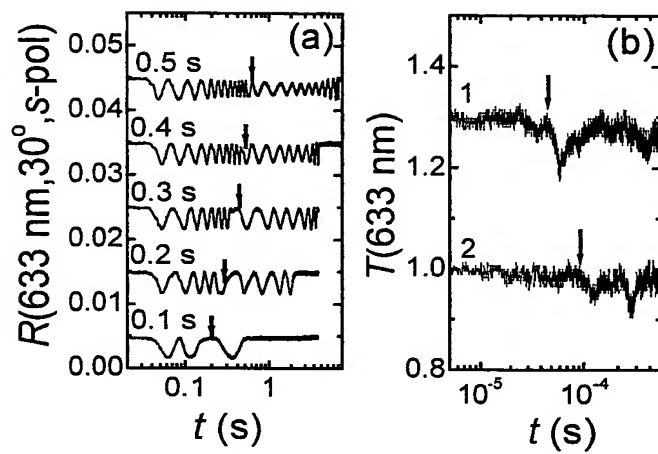


Fig.2, S.I. Kudryashov, Appl. Phys. Lett.

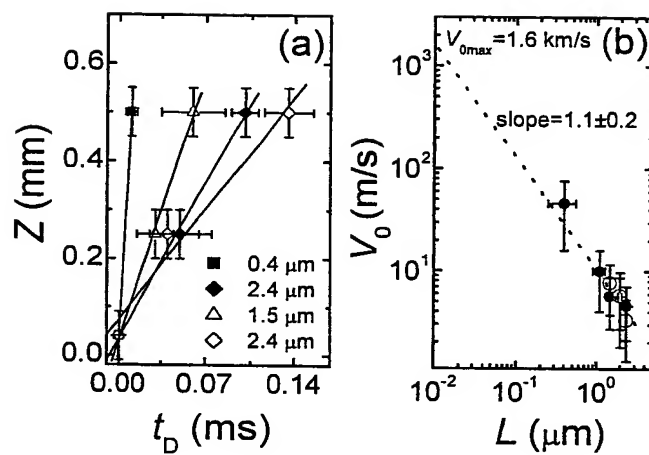


Fig.3, S.I. Kudryashov, Appl. Phys. Lett.